Catalysis Club of Philadelphia

Thursday October 22, 2009
Holiday Inn Select Hotel
Naamans Road and I-95, Claymont, DE

2009 Burwell Lecture:

Sponsored by Johnson Matthey

Restocking Burwell's Organometallic Zoo: Supported Metal Complexes and Metal Clusters with Well-Defined Structures

Prof. Bruce C. Gates
University of California, Davis

&

Controlling the Bond Scission Sequence of Methanol Decomposition on Platinum-Modified Tungsten Carbide

Alan L. Stottlemyer
University of Delaware
(Student Talk, 15 minutes)

Social Hour: 5:30 PM
Dinner: 6:30 PM
Meeting: 7:30 PM

Members: $30.00
Walk Ins & Non-members: $35.00
Student & Retired Members: $15.00

Menu

Chicken Hawaiian *- Served with Grilled Pineapple & Sweet and Sour Sauce*
Broiled Filet of Salmon *- Served with a Pomerey Mustard Sauce*
Vegan *- Penne Pommodoro*

Meal reservations - Please notify your company representative or Bill Lonergan (lonergan@udel.edu, phone: 518.369.6857, fax: 302.831.1048) by ***Thursday October 15***.

Company Representatives – We would like to encourage you to make meal/meeting reservations to your company representative.

Membership - Dues for the 2009-10 season will be $10.00 ($5.00 for the local chapter and $5.00 for the national club). Dues for students and post-docs will be $6.00 ($5.00 for local club and $1.00 for national club). Please send your payment to Steve Harris, LyondellBasell Industries 3801 West Chester Pike, Newtown Square, PA 19073-2387.

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Prof. Bruce C. Gates
Dept. of Chemical Engineering & Materials Science
University of California, Davis

Abstract

Robert Burwell was known for coining the term "organometallic zoo" to represent reaction intermediates on catalyst surfaces, and he pioneered work with catalysts consisting of metal complexes (e.g., molybdenum carbonyls) anchored to metal oxides. Extending his tradition, we have used organometallic precursors to prepare metal complexes and metal clusters on supports. Precursors that react precisely with structurally well-defined supports offer excellent opportunities for synthesis of uniform site-isolated catalysts that allow precise determinations of catalyst structure-property relationships. With complementary spectroscopic methods, such species can be characterized in the working state and as they undergo structural changes. This presentation is a summary of oxide- and zeolite-supported metal catalysts having virtually molecular properties. They have been synthesized from precursors incorporating reactive ligands such as acetylacetonate and ethylene and from supports that either facilitate characterization by high-resolution transmission electron microscopy (TEM) (MgO) or provide relatively uniform sets of binding sites for the supported species (zeolites). The characterization methods include IR, NMR, and X-ray absorption spectroscopies; high-resolution TEM; and density functional theory. The characterization results determine metal nuclearities, bonding of metals to supports, and identification of intermediates bonded to the metals. Comparisons of EXAFS and TEM data characterizing supported osmium clusters demonstrate quantitative agreement in the size determinations.

Results are presented for supported mononuclear complexes and clusters of ruthenium, rhodium, osmium, and iridium. For example, complexes of iridium bonded to ultrastable Y zeolite were prepared from the precursor $Ir(C_2H_4)_2(acac)$ [acac is $C_5H_7O_2$], giving supported $Ir(C_2H_4)_2$ complexes in which each Ir atom is bonded to two oxygen atoms of the zeolite. These complexes were imaged by aberration-corrected STEM. They were converted reversibly into clusters approximated as Ir_4, and the changes were followed in real time by XANES, EXAFS, and IR spectroscopies; the data indicate changes in the ligand spheres of the metal during the cluster formation and breakup, including evidence of changes in the metal–support interface, and they indicate how the catalyst structure can be tuned by choice of the reactant composition.

Supported catalysts with essentially molecular structure are an emerging class of materials that is expected to offer new reactivities and catalytic properties. Some of the lessons emerging from understanding of their structure and bonding appear to pertain to supported catalysts generally.

Burwell Award Announcement

The North American Catalysis Society is pleased to announce that Professor Bruce Gates is the recipient of the 2009 Robert Burwell Lectureship in Catalysis. Since 1992 Bruce has been on the faculty of the University of California at Davis, where he has the title of Distinguished Professor of Chemical Engineering. His interests include Catalysis, Catalytic Reactors, Chemical Reaction Engineering, Material Micro Structure, and Sol-Gel Processing.

This award is sponsored by Johnson Matthey Catalysts Company and administered by the Society. The award consists of a plaque and an honorarium as well as a travel award to provide the recipient with funds for visiting (until funds run out) any of the 14 local clubs comprising the Society. The award is given in recognition of substantial contributions to one or more areas in the field of catalysis with emphasis on discovery and understanding of catalytic phenomena, catalytic reaction mechanisms, and identification and description of catalytic sites and species.

For almost 40 years he has made significant contributions in three areas: the preparation and characterization of surface organometallic complexes, catalysis by strong solid acids, and the kinetics and reaction pathways of hydroprocessing catalysis. In the catalysis by strong solid acids, Bruce both expanded the applications and furthered understanding of underlying mechanisms. More recently, in a series of papers beginning in 1998, Bruce (with Bob Grasselli and Helmut Knözinger) explained the surface chemistry of tungstated zirconias with and without Pt, highlighting the role of surface reduction to W5+ and –OH in generating the active sites for alkane isomerization. Bruce's contributions to hydroprocessing catalysis are equally notable. His two review articles greatly assisted those requiring introduction to the field; each has been cited in excess of 375 times. The scientific contribution was his recognition (with James Katzer and George Schuit) that complex hydrodesulfurization and hydrogenation networks could be understood in terms of a small number of reactions whose rates could be quantified using model substrates. One supporter remarked that Bruce's work in metal clusters revolutionized the field of surface organometallic catalysis. Here also he has authored widely read reviews, and several influential, extensively cited papers. Much of this recent work has targeted catalysis by gold clusters or nanocrystals, work characterized by multi-technique correlation of catalytic activity to surface structure, careful interpretation of EXAFS data characterizing surface coordination, and proper consideration of how the catalysis alters the as-synthesized materials. Bruce was an early user and proponent of EXAFS and XANES in catalyst characterization. Many "nanoscience" papers in the literature today follow along paths he pioneered years ago.

Finally it should be noted that Bruce has educated two generations of catalytic scientists and industrial practitioners, through his widely used teaching texts ("Chemistry of Catalytic Processes" is a worldwide best seller), the many short courses he helped develop and teach (the one based on this book was taught for over 30 years at the University of Delaware, and at many industrial research centers) and not least through his mentoring of over 130 graduate students, postdocs and visiting scientists. Bruce has been a tireless cheerleader for the field of catalysis and in all his lectures strives for understanding, arousing curiosity, and getting down to the essentials of a problem. He has also been a very active member of the Board of the North American Catalysis Society.

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Controlling the Bond Scission Sequence of Methanol Decomposition on Platinum-Modified Tungsten Carbide

Alan L. Stottlemyer, Ping Liu, Jingguang G. Chen
Department of Chemical Engineering, University of Delaware
(Student Talk, 15 minutes)

Abstract

The direct methanol fuel cell (DMFC) directly converts the chemical energy of methanol into electrical energy. While methanol fuel cells are favored by many electrochemists for their high power density as compared to hydrogen fuel cells, the electrooxidation of methanol results in a CO intermediate that forms strong bonds with Pt, which is widely accepted as the most appropriate DMFC electrocatalyst.[1] This can lead to surface poisoning and eventual catalyst deactivation; thus, a more CO tolerant electrocatalytic material will facilitate the commercialization of DMFC. Recent studies have suggested that tungsten monocarbide (WC) may behave similarly to Pt for the electrooxidation of methanol.[2,3] Temperature programmed desorption (TPD) was used to quantify the activity and selectivity of methanol decomposition for WC and platinum-modified WC (Pt/WC) as compared to Pt.[4] While WC appeared to be more active than Pt in ultra-high vacuum (UHV), C-O bond scission resulted in gas phase CH_4, an undesired reaction for DMFC. When Pt is added to WC by physical vapor deposition, the CH_4 reaction pathway is significantly reduced, suggesting that Pt synergistically modifies WC to improve the selectivity for reforming products. Additionally, TPD confirmed WC and Pt/WC to be more CO tolerant than Pt.[5] Density functional theory (DFT) was used to study the reaction network of methanol on Pt/WC(0001) as compared to Pt(100) and WC(0001). Results suggested that the bond scission sequence of CH_3OH could be controlled using submonolayer coverages of Pt on WC and that the resulting mechanism was different for Pt/WC as compared to either parent surface. High-resolution electron energy loss spectroscopy (HREELS) verified that surface intermediates were different on Pt/WC as compared to Pt or WC and that methanol decomposition occured at lower temperatures for the WC surfaces. Ultimately, this study suggests that Pt-modified carbide surfaces can be used to control the bond scission sequence of small oxygenates and that WC is a more CO tolerant material than Pt; thus, WC and Pt/WC could be promising alternatives to Pt electrocatalysts for low temperature fuel cells.

[1] L. Carrette, K. Friedrich, U. Stimming, *Fuel Cells* **2001**, *1*, 5.
[2] H. Hwu, J. Chen, *Chemical Reviews* **2005**, *105*, 185.
[3] E. Weigert, A. Stottlemyer, M. Zellner, J. Chen, *Journal of Physical Chemistry C* **2007**, *111*, 14617.
[4] A. Stottlemyer, P. Liu, J. Chen, *In Preparation* **2009**.
[5] Z. Mellinger, E. Weigert, A. Stottlemyer, J. Chen, *Electrochemical and Solid-State Letters* **2008**, *11*, B63.

Speaker's Bio

After graduating from a small-town high school outside of Tampa, FL, Alan began his undergraduate studies at the University of Florida in 2000. While at Florida, he studied heat and mass transfer in non-linear, bi-furcated systems under the advisement of Dr. Ranga Narayanan. Alan obtained a B.S. in Chemical Engineering and a B.A. in Spanish in 2005. Later the same year he matriculated at the University of Delaware, where he is now in his fifth year of study with Dr. Jingguang Chen. His thesis research focuses on surface science and density functional theory studies of the fundamentals of oxygenate decomposition on bimetallic and transition metal carbide surfaces.